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(19)(CA) **APPLICATION FOR CANADIAN PATENT** (12)

(54) Treatment of Filtrates in Peroxide Bleaching of Pulp

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(30) (US) 08/435,290 1995/05/05

(57) 20 Claims

ABSTRACT OF THE DISCLOSURE

Cellulose (paper) pulp is bleached by first washing it in a first washing stage using a first wash liquid, passing the pulp from the first washing stage to a peroxide bleaching stage (either unpressurized or at superatmospheric pressure), after the peroxide bleaching stage washing the cellulose pulp in a second washing stage using a second wash liquid and producing a filtrate, and then treating the filtrate and bringing the filtrate to the first washing stage to be used as the wash liquid in it. The filtrate is treated by bringing it into intimate contact with an oxidizing gas to oxidize contaminants in it. The method typically includes an ozone bleaching stage either before or after the peroxide stage, in which ozone containing gas is used to bleach the pulp and produces an off gas containing residual amounts of ozone (typically in an oxygen carrier gas). This off gas with residual ozone (which may be supplemented by ozone from a low cost ozone generator) is preferably used as the oxidizing gas for the filtrate, and can be used to remove odors from other pulp mill fluid streams. The filtrate may be treated in a vertical tank having a gas sparger at the bottom in which case the oxidizing gas is introduced into the vertical tank through the gas sparger, and the tank is maintained at either atmospheric or superatmospheric pressure. Alternatively a gas scrubber, or other conventional gas-liquid contactor, can be used to treat the filtrate.

TREATMENT OF FILTRATES IN PEROXIDE BLEACHING OF PULP

BACKGROUND AND SUMMARY OF THE INVENTION

In continuing efforts to reduce the environmental impact associated with the production of kraft pulp, a number of techniques have been developed to "close" a bleaching system of a kraft pulping facility so that there is no or very little discharge of washing filtrates into the environment. These bleaching systems essentially eliminate chlorine and use in place of chlorine more environmentally friendly bleaching agents such as ozone and peroxide. For example co-pending application serial no. 07/861,387 filed March 31, 1992, and co-pending application serial no. 08/031,432 filed March 15, 1993, teach various mechanisms for handling filtrates in bleaching cellulose pulp. According to the FIGURE 3 embodiment of these applications filtrate used for washing the pulp in a washing stage prior to an ozone bleaching stage is oxidized as by purifying the off gas from the ozone bleaching stage so that essentially only the carrier gas (typically oxygen, but also potentially air) is used in a reactor, with alkali, to remove contaminants from the filtrate prior to the washing stage.

It has now been found according to the present invention that there are other situations in a pulp mill bleach plant which can benefit from oxidizing the filtrate. For example it has been recognized according to the present invention that pulp brightness may be adversely affected when peroxide stage filtrate (from a washing stage after a peroxide bleaching stage) is routed back to a washer ahead of the P stage to be used as wash liquid in the earlier

washing stage. This filtrate may have a yellowish color, which eventually carries through with the bleached pulp, having contaminants, particularly organics, therein which adversely affect the pulp brightness.

According to the present invention the pulp brightness problem recognized above is solved by oxidizing the filtrate prior to its being used as a wash liquid before a P-stage. This oxidizing is particularly effective when the filtrate is treated with the off gas from an ozone bleach stage which contains the carrier gas (typically oxygen) and a residual amount of ozone, typically about one percent or less, if the oxidizing gas is brought into intimate contact with the filtrate. This gas is also useful in other processes, such as to treat condensates to remove odors, and to treat off-gases from a pulp mill chemical recovery systems to remove odors. An alternative source of oxidizing agent is a low concentration, low pressure ozone gas that can be obtained from a commercially available, low cost (low ozone concentration capability, e.g. 4% or less) ozone generator.

According to the present invention a method of bleaching cellulose pulp is provided comprising the steps of continuously: (a) Washing kraft cellulose pulp in a first washing stage using a first wash liquid. (b) Passing the pulp from the first washing stage to a peroxide bleaching stage. (c) After the peroxide bleaching stage, washing the pulp in a second washing stage using a second wash liquid, and producing a filtrate. (d) Bringing the filtrate from the second washing stage into intimate contact with an oxidizing gas to oxidize contaminants therein to produce a purified filtrate. And, (e) after step (d), using the purified filtrate as the first wash liquid in step (a). The washing steps (a) and (c) may also include pressing to increase consistency.

According to a preferred embodiment of the invention there is the further step (f) of before the first washing stage, or after the second washing stage, bleaching the pulp in an ozone stage using ozone containing gas, to produce an off gas containing residual amounts of ozone therein; and step (d) is preferably practiced using the off gas from step (f) as at least part of the oxidizing gas. The method may be practiced utilizing a vertical tank having a gas sparger at the bottom thereof, in which case step (d) is practiced by introducing the oxidizing gas into the vertical tank through the gas sparger. The tank may be maintained at substantially atmospheric pressure, or at superatmospheric pressure (e.g. about 2 bar or above). Alternatively instead of a tank with gas sparger a conventional gas scrubber, or any suitable conventicnal liquid-gas contacting device, may be utilized.

In the practice of the method there is typically the further step of subjecting the pulp, either before or after the peroxide stage, to at least one other bleaching stage. Typically the steps (a) through (e) are practiced with the cellulose pulp at a consistency throughout of about 6-18%, and the ozone bleaching is also preferably carried out at this medium consistency. The peroxide bleaching stage may be of superatmospheric pressure peroxide bleaching stage, the pressure being at least 2 bar.

According to another aspect of the present invention a cellulose pulp treating apparatus is provided. The apparatus comprises the following components: A first wash stage including a first wash liquid inlet. A peroxide bleaching stage connected to the first wash stage, washed pulp passing from the first wash stage to the peroxide bleaching stage. A second wash stage including a second wash liquid inlet, and a filtrate outlet, the peroxide bleaching stage connected to the second wash stage so that pulp passing from the peroxide

bleaching stage passes to the second wash stage. A vertical tank having a gas sparger adjacent the bottom thereof, a liquid inlet, and a liquid outlet. A source of oxidizing gas connected to the gas sparger. The filtrate outlet connected to the tank liquid inlet. And, the tank liquid outlet connected to the first wash stage wash liquid inlet.

The apparatus preferably further comprises an ozone bleaching stage including an off-gas outlet for carrying carrier gas (typically oxygen) with a residual amount of ozone gas (typically about one percent or less) away from the ozone bleaching stage. The off-gas outlet of the ozone bleaching stage preferably is the source of the oxidizing gas connected to the gas sparger. If the ozone-containing off-gases from an ozone bleaching stage are not sufficient to oxidize the filtrate, the off-gases may be supplemented by other sources of oxidizing agents. For example, ozone from a low cost ozone generator may be used.

According to another aspect of the present invention there is provided a method of treating a fluid of a pulp mill to remove color or odor therefrom, the mill including at least one ozone bleaching stage having off-gases therefrom. This method comprises the steps of: (a) removing the off-gases from the at least one ozone bleaching stage, the off gases having residual ozone therein at a concentration of 4% or less (e.g. 1% or less) in a carrying gas including oxygen; and (b) without intermediate treatment which destroys the residual ozone bringing the off-gases from step (a) into intimate contact with a pulp mill fluid having adverse odor or color or both so that the ozone is completely consumed, and so that the odor or color or both are reduced.

Step (b) may be practiced to bring the off-gases into contact with a pulp mill liquid condensate having undesirable odor, or to

bring the off-gases into contact with a gaseous discharge from a piece of equipment associated with the chemical recovery loop (e. g. a recovery boiler, smelt dissolver, or lime kiln), or as described in detail above, by bringing the off-gases into contact with a filtrate from a washer after a peroxide bleaching stage, using a tank with gas sparger or a gas scrubber.

It is the primary object of the present invention to effectively treat cellulose pulp utilizing peroxide as one of the bleaching stages, while properly reutilizing the filtrates from various wash stages yet not adversely affecting the bleaching of the pulp because of recycled filtrate use, and to treat fluids from a pulp mill with off gas from an ozone bleaching stage to remove color and/or odor while simultaneously using up the residual ozone. This and other objects of the invention will become clear from an inspection of the detailed description of the invention, and from the appended claims.

BRIEF DESCRIPTION OF THE DRAWINGS

FIGURE 1 is a schematic view of an exemplary bleaching method for cellulose pulp according to the present invention;

FIGURE 2 is a schematic view showing the particulars of one embodiment of the filtrate treating apparatus of the system of FIGURE 1;

FIGURE 3 is a view like that of FIGURE 2 of an alternative construction of the filtrate treating apparatus according to the invention; and

FIGURES 4 and 5 are schematic views of other systems according to the invention for using the off-gases from a Z stage, with residual ozone, to treat a pulp mill fluid having undesirable odor and/or color.

DETAILED DESCRIPTION OF THE DRAWINGS

FIGURE 1 schematically illustrates a system utilized for practicing the method of treating/bleaching cellulose pulp according to the present invention. The pulp is typically kraft pulp, and is provided in line 10 at a consistency that is typically about 6-18%. The pulp may optionally first be treated in one or more first bleaching stages 11 which typically use non-chlorine bleaching chemicals, and the pulp is subjected to washing in a first washing stage 12 in which a first wash liquid is introduced through inlet 13, and the filtrate exits the wash stage 12 in line 14. The filtrate in line 14 may be used in earlier washing stages, or it may be treated, used as make-up liquid at other parts of the bleach plant or pulp mill, or handled in other manners.

After the first washing stage 12 the pulp passes substantially immediately to a peroxide bleaching stage 15. The stage 15 may either be an atmospheric peroxide stage or a superatmospheric stage, and the peroxide typically used is hydrogen peroxide, and it is used at known or conventional temperatures, and charges. The pulp is typically also at medium consistency when bleached in the stage 15. After the stage 15 the pulp passes substantially immediately to a second wash stage 16 which has a wash liquid inlet 17 and a filtrate outlet 18. The wash liquid added in line 17 may be fresh water, or from a downstream bleaching stage. Stages 12 and 16 may include pressing to increase consistency, and/or may be practiced by any

color, but also other contaminants) therein so that the liquid introduced as a wash liquid in inlet 13 is a relatively clean liquid.

A preferred embodiment of the apparatus 23 is illustrated schematically, but in more detail, in FIGURE 2. The apparatus 23 includes a vertical tank 25 having a gas sparger 26 at the bottom thereof. The filtrate is introduced into the tank 25, e.g. adjacent the bottom thereof, from line 18 as illustrated in FIGURE 2, while the purified filtrate exits from the top of the tank 25, to pass to the inlet 13 as also illustrated in FIGURE 2. The tank 25 may be at substantially atmospheric pressure, or may be held under superatmospheric pressure (e.g. about 2 bar or above). The oxidizing gas from source 27 is introduced into the gas sparger 26 to move into intimate contact with the filtrate in the tank 25. The oxidizing gas source 27 -- as illustrated schematically in FIGURE 1 – preferably comprises the off-gases in line 21 from the ozone stage 19, which contains a residual amount of ozone. If the amount of residual ozone is insufficient for complete oxidation it may be enhanced by ozone from a conventional low cost ozone generator 22 (see FIGURE 1); the low cost generator 22 may not be able to produce an ozone concentration of more than 4% and thus is not suitable for producing ozone for stage 19, but that is entirely sufficient for purposes of the invention. The ozone is a very effective oxidizing agent, and since there is a significant residence time in tank 25 (e.g. at least about 30 seconds, typically significantly more, such as several minutes), all of the ozone is consumed, therefore eliminating the need for further treatment. At the top of the tank 25 remaining gases may be exhausted as indicated by reference numeral 29, or the purified filtrate may pass through a degasser before being introduced into the inlet 13.

If desired, a heat exchanger can be provided between the various flows [as illustrated in FIGURE 3 of co-pending application serial no. 07/861,387 filed March 31, 1992]. Also if it is necessary to adjust the pH of the wash liquid, this can also be done by adding acid or alkali to the tank 25, or to the filtrate in line 18 just before the tank 25, good mixing taking place in the tank 25.

FIGURE 3 illustrates another embodiment that the apparatus 23 can take, in FIGURE 3 the apparatus being shown generally by reference numeral 23'. In this embodiment a conventional gas scrubber 32 is utilized, oxidizing gas from source 27 (which, again, may be the line 21 from ozone stage 19) being scrubbed with the filtrate introduced in line 18, as is conventional. A gas outlet 33 may also be provided. Any conventional scrubber 32 can be used, one in which the gas to be scrubbed is introduced at the top, or at the bottom (as illustrated in FIGURE 3). Alternatively, other suitable conventional liquid-gas contacting devices can be used instead of structures 25, 32.

While in the preferred embodiment the pulp is at medium consistency (about 6-18%) throughout the entire treatment seen in FIGURE 1, where particular stages may be practiced better at different consistencies, pressing, thickening, or diluting apparatus may be utilized.

FIGURE 4 illustrates another manner in which the off-gases from the ozone (Z) stage 19 may be used advantageously in a cellulose pulp mill. The mill includes an evaporator 40, or a like piece of equipment (e. g. condenser, or condensing part of other equipment) which produces a condensate in line 41. The liquid condensate in line 41 is brought into intimate contact with the off-gases containing residual ozone [of 4% or less, typically about 1% or less, in an oxygen containing carrier gas, such as pure oxygen or air]

in line 21 (the gases in line 21 not being treated to remove the residual ozone), as in contactor 42. The contactor 42 may be a tank with gas sparger like the apparatus 23, or a gas scrubber like the apparatus 23', or a simple mixer, or a wide variety of other conventional structures. The ozone, and perhaps other oxidizing elements of the gas in line 21, is consumed, removing at least some of the odor from the condensate in line 41, producing a substantially odor-free condensate in line 43. Remaining gas may be exhausted in line 44, or may be removed from the condensate in line 43 by a degasser, or the like.

FIGURE 5 shows a system similar to that of FIGURE 4 for treating odor-containing off-gases from a piece of equipment 48 from the pulp mill chemical recovery plant, such as a recovery boiler, lime kiln, or smelt dissolver. The odoriferous gas in line 49 is mixed with the off-gas (containing residual ozone) in line 21, e. g. in a mixer 50 or other contactor, the ozone and perhaps other oxidizing elements of the gas in line 21 removing at least some of the odor from the gas in line 49, producing relatively odor-free gas in line 51, which may be further treated, or discharged to the environment, or used as a combustion gas in the recovery boiler or the like.

It will thus be seen that according to the present invention a method and apparatus have been provided which enhance the brightness of pulp produced utilizing a peroxide bleaching stage, while effectively reusing filtrates so as to minimize the amount of undesirable discharges to the environment. The invention also effectively utilize the off-gases from an ozone bleaching stage so that those off-gases need not be further specially treated in order to discharge them into the environment.

While the invention has been herein shown and described in what is presently conceived to be the most practical and preferred

embodiment thereof it will be apparent to those of ordinary skill in the art that many modifications may be made thereof within the scope of the invention, which scope is to be accorded the broadest interpretation of the appended claims so as to encompass all equivalent methods and apparatus.

WHAT IS CLAIMED IS:

1. A method of treating kraft cellulose pulp, comprising the steps of continuously:

(a) washing kraft cellulose pulp in a first washing stage using a first wash liquid;

(b) passing the pulp from the first washing stage to a peroxide bleaching stage;

(c) after the peroxide bleaching stage, washing the pulp in a second washing stage using a second wash liquid, and producing a filtrate;

(d) bringing the filtrate from the second washing stage into intimate contact with an oxidizing gas to oxidize contaminants therein to produce a purified filtrate; and

(e) after step (d), using the purified filtrate as the first wash liquid in step (a).

2. A method as recited in claim 1 comprising the further step (f) of before the first washing stage, or after the second washing stage, bleaching the pulp in an ozone stage using ozone containing gas, to produce an off gas containing residual amounts of ozone therein; and wherein step (d) is practiced using the off gas from step (f) as at least part of the oxidizing gas, the residual ozone consumed during the practice of step (d).

3. A method as recited in claim 2 using a vertical tank having a gas sparger at the bottom thereof; and wherein step (d) is practiced by introducing the oxidizing gas into the vertical tank through the gas sparger.

4. A method as recited in claim 2 using a gas scrubber; and wherein step (d) is practiced by introducing the filtrate and the oxidizing gas into the gas scrubber.

5. A method as recited in claim 3 wherein step (d) is practiced under superatmospheric pressure.

6. A method as recited in claim 3 wherein step (d) is practiced substantially at atmospheric pressure.

7. A method as recited in claim 3 wherein the off gas comprises primarily oxygen gas, with about 4% or less ozone therein.

8. A method as recited in claim 2 comprising the further step of supplementing the ozone in the gas in step (f) with ozone from a low cost ozone generator having the capability of producing ozone at a maximum concentration of about 4%.

9. A method as recited in claim 1 using a vertical tank having a gas sparger at the bottom thereof; and wherein step (d) is practiced by introducing the oxidizing gas into the vertical tank through the gas sparger.

10. A method as recited in claim 1 using a gas scrubber; and wherein step (d) is practiced by introducing the filtrate and the oxidizing gas into the gas scrubber.

11. A method as recited in claim 2 wherein the off gas comprises primarily oxygen gas, with about 4% or less ozone therein.

12. A method as recited in claim 1 comprising the further step of subjecting the pulp, either before or after the peroxide bleaching stage, to at least one other bleaching stage.

13. A method as recited in claim 2 wherein the off gas from step (f) comprises a gas at a pressure of less than about 2 bar, and with an ozone concentration of about 1% or less.

14. A method as recited in claim 1 wherein steps (a)-(e) are practiced with the cellulose pulp at a consistency throughout of about 6-18%.

15. A method of treating a fluid of a pulp mill to remove color or odor therefrom, the mill including at least one ozone bleaching stage having off-gases therefrom, said method comprising the steps of:

(a) removing the off-gases from the at least one ozone bleaching stage, the off gases having residual ozone therein at a concentration of 4% or less in a carrying gas including oxygen; and

(b) without intermediate treatment which destroys the residual ozone bringing the off-gases from step (a) into intimate contact with a pulp mill fluid having adverse odor or color or both so that the ozone is completely consumed, and so that the odor or color or both are reduced.

16. A method as recited in claim 15 wherein step (b) is practiced to bring the off-gases into contact with a pulp mill liquid condensate having undesirable odor.

17. A method as recited in claim 15 wherein step (b) is practiced to bring the off-gases into contact with a gaseous discharge from a recovery boiler, smelt dissolver, or lime kiln.

18. A method as recited in claim 15 wherein step (b) is practiced by bringing the off-gases into contact with a filtrate from a washer after a peroxide bleaching stage, using a tank with gas sparger or a gas scrubber.

19. Cellulose pulp treating apparatus, comprising:

a first wash stage including a first wash liquid inlet;

a peroxide bleaching stage connected to said first wash stage, washed pulp passing from said first wash stage to said peroxide bleaching stage;

a second wash stage including a second wash liquid inlet, and a filtrate outlet, said peroxide bleaching stage connected to said second wash stage so that pulp passing from said peroxide bleaching stage passes to said second wash stage;

a vertical tank having a gas sparger adjacent the bottom thereof, a liquid inlet, and a liquid outlet;

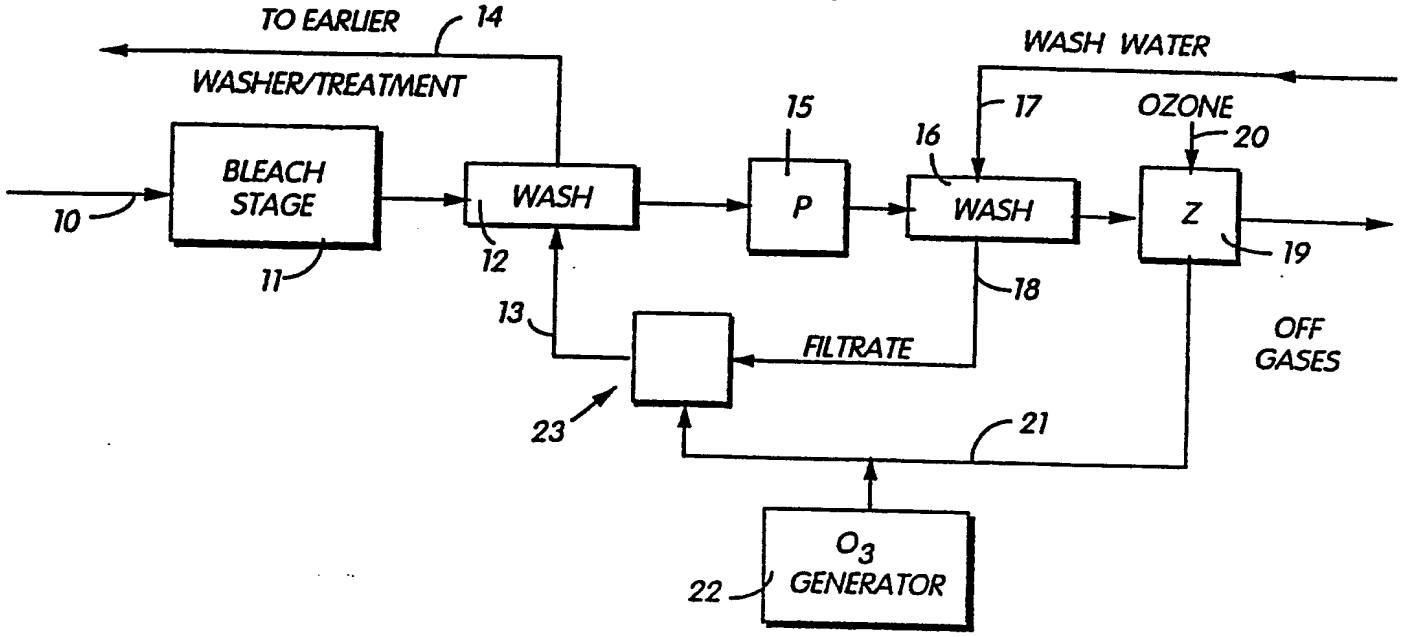
a source of oxidizing gas connected to said gas sparger;

said filtrate outlet connected to said tank liquid inlet; and

said tank liquid outlet connected to said first wash stage wash liquid inlet.

20. Apparatus as recited in claim 19 further comprising an ozone bleaching stage including an off-gas outlet for carrying carrier gas with a residual amount of ozone gas away from said ozone bleaching stage; and wherein said off-gas outlet of said ozone bleaching stage is said source of oxidizing gas.

FIG. 1



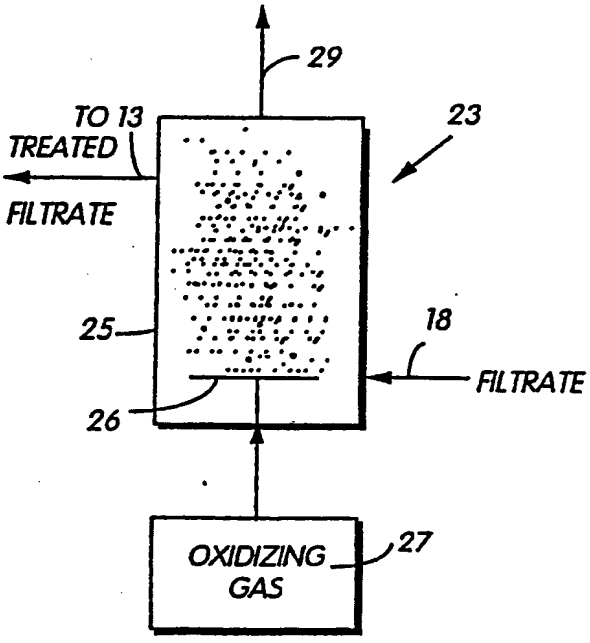


FIG. 2

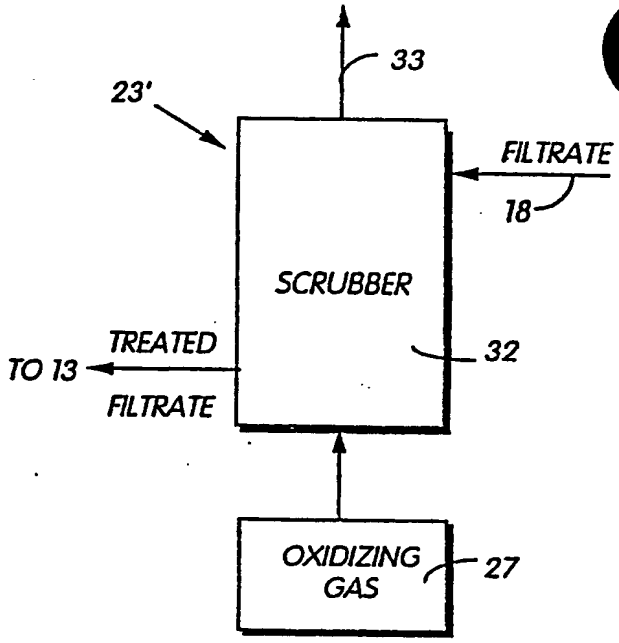
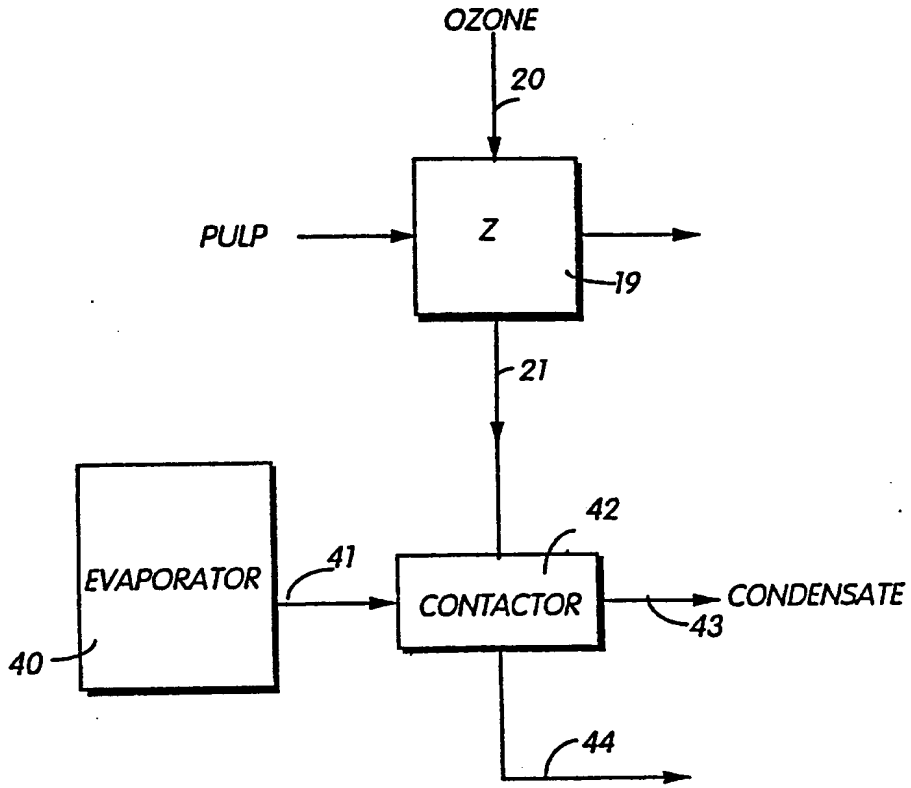


FIG. 3

FIG. 4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PULP
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EVAPORATOR
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CONTACTOR
CONDENSATE
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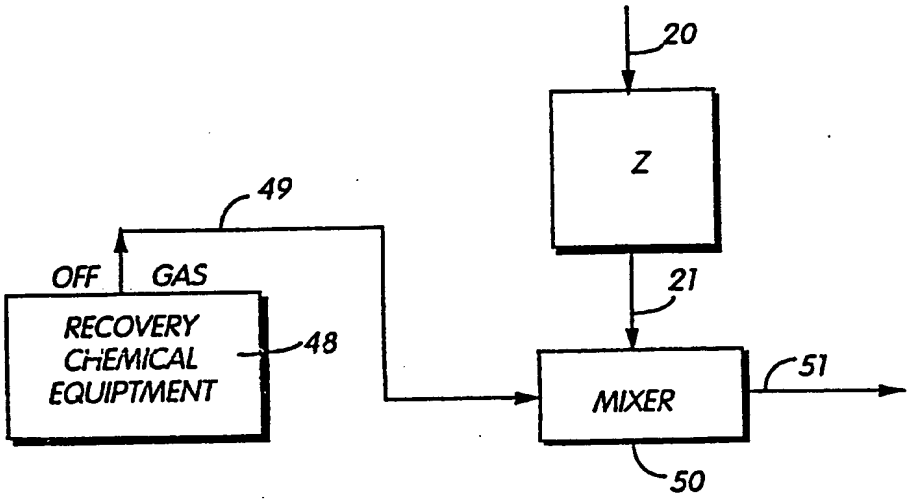
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RECOVERY
CHEMICAL
EQUIPTMENT
48
MIXER
51
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FIG. 5